

VINYL CHLORIDE FIBER AND METHOD OF SAME

REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of Japanese Patent Application No. 2003-345440 filed on October 3, 2003, and to Japanese PCT Application No. PCT/JP2004/013215 filed on September 10, 2004.

TECHNICAL FIELD

[0002] The present invention relates to a vinyl chloride fiber having a gloss, hue and appearance similar to human hair, and utilized for manufacturing hair ornament products such as wig, hairpiece, braid, and extension hair.

RELATED ART

[0003] A vinyl chloride fiber spun from a vinyl chloride resin has an excellent transparency and flexibility so that the vinyl chloride fiber is conventionally utilized for artificial hair fibers of hair ornament products. For a manufacturing of the artificial hair fiber, there are two methods with regard to solvent. One is wet or dry spinning, which utilizes solvent and the other is melt spinning, which does not utilize solvent.

[0004] The vinyl chloride resin has a high melting viscosity and a low stringiness so that it is difficult to melt spinning the vinyl chloride resin and manufacture the vinyl chloride fiber with a certain quality. When the vinyl chloride resin is exposed to hot environment, sunlight or ultraviolet rays, a vinyl chloride polymer, which constitutes the vinyl chloride resin, is dehydrochlorinated. As a result, the vinyl chloride fiber formed with the vinyl chloride resin has a poor initial coloring property and shows an yellow color so that the product value is reduced.

[0005] JP,H11-100714,A discloses a process of producing a vinyl chloride fiber comprising a vinyl chloride resin composition having (a) 1-35 parts by weight of an ethylene-vinyl acetate resin, (b) 0.2-5.0 parts by weight of a thermal stabilizer, and (c) 0.2-5.0 parts by weight of a lubricant, to 100 parts by weight of a vinyl chloride mixture consisting of 100-60wt% of a vinyl chloride resin and 0-40wt% of a chlorinated vinyl chloride resin. JP,H11-100714,A also discloses that the thermal

stabilizer is selected at least one from a tin-thermal stabilizer, a Ca-Zn thermal stabilizer, a hydrotalcite thermal stabilizer, and a zeolite thermal stabilizer.

[0006] However, when the tin-thermal stabilizer (organotin stabilizer) is utilized for the melt spinning of the vinyl chloride resin composition and discharged to environment, they cause adverse effect on ecosystem and release a peculiar odor. When the other thermal stabilizers than the tin-thermal stabilizer are added to the vinyl chloride resin composition, a thread breakage of the vinyl chloride fiber often occurs during manufacturing and the vinyl chloride fiber manufactured has a poor initial coloring property.

[0007] When the hydrotalcite thermal stabilizer is utilized for the melt spinning of the vinyl chloride resin composition, carbides of the vinyl chloride resin stick to a metal net in the melt spinning apparatus and cause frequently the thread breakage of the fiber so that the continuous or long-run melt spinning is disturbed. The vinyl chloride fiber containing the hydrotalcite thermal stabilizer changes a color thereof when the fiber is curled with heat.

## DISCLOSURE OF THE INVENTION

[0008] The present invention is to provide a vinyl chloride fiber, which does not change a color when it is curled, and a method of manufacturing the same utilizing a hydrotalcite thermal stabilizer. The method provides a stable melt spinning and productivity.

[0009] From our study on the problems described above, that is, the sticking of the carbides of the vinyl chloride resin to the metal net during melt spinning the vinyl chloride resin composition containing the hydrotalcite thermal stabilizer, and the color change of the vinyl chloride fiber, which contains the hydrotalcite thermal stabilizer, when the fiber is curled, it is found that these problems are caused by an improper dispersion of the hydrotalcite thermal stabilizer. In the present invention, (c) 0.2-10.0 parts by mass of an epoxy compound is added to a vinyl chloride resin composition containing (a) 100 parts by mass of a vinyl chloride resin and (b) 0.2-5.0 part by mass of a hydrotalcite thermal stabilizer. As a result, a long-run melt spinning and a stable productivity are achieved for the vinyl chloride fiber even though the hydrotalcite thermal stabilizer is added. The resulting fiber does not change the color when the fiber is curled at a curling process.

**[0010]** According to a first aspect of the present invention, a vinyl chloride fiber consists of a vinyl chloride resin composition including (a) 100 parts by mass of a vinyl chloride resin, (b) 0.2-5.0 parts by mass of a hydrotalcite thermal stabilizer and (c) 0.2-10.0 parts by mass of an epoxy compound.

**[0011]** Preferably, the epoxy compound is at least one compound selected from an epoxidized animals and plants oil, such as epoxidized soybean oil, epoxidized linseed oil, epoxidized tung oil, epoxidized fish oil, epoxidized beef tallow oil, epoxidized castor oil and epoxidized safflower oil, and epoxy-containing methacrylic acid compound, epoxidized methyl stearate, epoxidized polybutadiene, tris (epoxy propyl) isocyanurate, epoxidized tallol oil fatty ester, epoxidized linseed oil fatty ester, vinylcyclohexene diepoxide, dicyclohexene carboxylate, diglycidyl ether of bisphenol A, glycerin polyglycidyl ether, and cyclohexane dimethanol polyglycidyl ether.

**[0012]** Preferably, the vinyl chloride resin composition contains (d) 0.01-2.0 parts by mass of a nitrogen-containing polyol.

**[0013]** Preferably, the nitrogen-containing polyol is tris (2-hydroxyethyl) isocyanurate, tris (3-hydroxypropyl) isocyanurate, or tris (4-hydroxybutyl) isocyanurate.

**[0014]** According to a second aspect of the present invention, a method of manufacturing a vinyl chloride fiber includes the steps of: forming a vinyl chloride resin composition with (a) 100 parts by mass of a vinyl chloride resin, (b) 0.2-5.0 parts by mass of a hydrotalcite thermal stabilizer, and (c) 0.2-10.0 parts by mass of an epoxy compound; and melt spinning said vinyl chloride resin composition at a temperature of 170-190°C.

**[0015]** Preferably, the method further includes the steps of: stretching said vinyl chloride fiber melt spun to 2 to 4 times at an environment temperature of 90-120°C; and keeping the vinyl chloride fiber stretched at an environment temperature of 110-140°C until a length thereof becomes 60-100% of a original length.

**[0016]** Preferably, the vinyl chloride resin composition contains (d) 0.01-2.0 parts by mass of a nitrogen-containing polyol.

## BEST MODE FOR CARRYING OUT THE INVENTION

[0017] A vinyl chloride fiber is formed from a vinyl chloride resin composition including (a) 100 parts by mass of a vinyl chloride resin, (b) 0.2-5.0 parts by mass of a hydrotalcite thermal stabilizer, and (c) 0.2-10.0 parts by mass of an epoxy compound.

[0018] As a result, even though the hydrotalcite thermal stabilizer is included, a long-run melt spinning and stable productivity for the vinyl chloride fiber are achieved and a color change thereof does not occur when a heat is applied to the fiber at a curling process.

[0019] The vinyl chloride resin includes (1) resins formulated from bulk, solution, suspension and emulsion polymerization of a vinyl chloride, but not limited to the steps, such as polyvinyl chloride, chlorinated polyvinyl chloride, polyvinylidene chloride, chlorinated polyethylene, vinyl chloride-acetic acid vinyl copolymer, vinyl chloride-ethylene copolymer, vinyl chloride-propylene copolymer, vinyl chloride-styrene copolymer, vinyl chloride-isobutylene copolymer, vinyl chloride-vinylidene chloride copolymer, vinyl chloride-styrene-maleic anhydride terpolymer, vinyl chloride-styrene-acrylonitrile terpolymer, vinyl chloride-butadiene copolymer, vinyl chloride-isoprene copolymer, vinyl chloride-chlorinated propylene copolymer, vinyl chloride-vinylidene chloride-acetic acid vinyl terpolymer, vinyl chloride-maleic acid ester copolymer, vinyl chloride-methacrylic acid ester copolymer, vinyl chloride-acrylonitrile copolymer, vinyl chloride-several vinyl ether copolymers, (2) blends among the resins of (1), (3) synthetic resins not containing the above and chlorine, such as acrylonitrile-styrene copolymer, acrylonitrile-styrene-butadiene terpolymer, ethylene-acetic acid vinyl copolymer, ethylene-ethyl (meta) acrylate copolymer, blends with polyester, and (4) vinyl chloride-polymerized containing block copolymer and graft copolymer.

[0020] The vinyl chloride resin composition for manufacturing the fiber may contain known additives utilized for the vinyl chloride composition, such as plasticizer, lubricant, compatible agent, processing assist, strengthening agent, ultraviolet absorption agent, oxidization prevention agent, anti-electric agent, filler, flame retardant, pigment, initial coloring improvement agent, conductive grant agent, finishing agent, optical stabilizer, and spice.

[0021] The vinyl chloride fiber of the present invention has a diameter of 20-100 denier, or preferably 50-80 denier. The fiber with the diameter of 20-100 denier

appears like natural human hair and the fiber of 50-80 denier has an improved tactile impression and appearance.

**[0022]** A cross section of the vinyl chloride fiber of the present invention may have either one or the combination of circular, ellipse, glasses, star, H, T, Y, triangle, quadrangle, cross, heart, horseshoe shapes, or may be hollow.

**[0023]** Contrary to organic tin thermal stabilizers, the hydrotalcite thermal stabilizer of the present invention does not have toxicity and yield adverse effect to microbes in environment and generate an odor. The hydrotalcite thermal stabilizer is a hydrotalcite compound. The hydrotalcite compound is a complex compound containing magnesium and/or alkaline metal, aluminum or zinc, magnesium and aluminum. The compound may dehydrated. The hydrotalcite compound can be either natural products or synthetic compounds synthesized by any known methods.

**[0024]** In the present invention, if the hydrotalcite thermal stabilizer is less than 0.2 parts by mass, a thread breakage of the fiber frequently occurs. When the hydrotalcite thermal stabilizer is more than 5.0 parts by mass, the initial coloring becomes worse. Accordingly, the suitable amount of the hydrotalcite is 0.2 to 5.0 parts by mass, preferably 0.5 to 3.0 parts by mass.

**[0025]** The "epoxy compound" of the present invention is preferably at least one compound selected from an epoxidized animals and plants oil, such as epoxidized soybean oil, epoxidized linseed oil, epoxidized tung oil, epoxidized fish oil, epoxidized beef tallow oil, epoxidized castor oil and epoxidized safflower oil, and epoxy-containing methacrylic acid compound, epoxidized methyl stearate, epoxidized polybutadiene, tris (epoxy propyl) isocyanurate, epoxidized tallol oil fatty ester, epoxidized linseed oil fatty ester, vinylcyclohexene diepoxide, dicyclohexene carboxylate, diglycidyl ether of bisphenol A, glycerin polyglycidyl ether, and cyclohexane dimethanol polyglycidyl ether. Any epoxy compounds can be utilized as far as they are acceptable.

**[0026]** When the amount of the epoxy compound is less than 0.2 parts by mass, the stable long-run melt spinning and the color change depression effect are reduced. When the epoxy compound is more than 10.0 parts by mass, the thread breakage frequently occurs. Accordingly, the preferable amount of the epoxy compound is 0.2 to 10.0 parts by mass, preferably 0.5 to 3.0 parts by mass.

**[0027]** In the present invention, preferably, the vinyl chloride resin composition further contains (d) 0.01 to 2.0 parts by mass of a nitrogen-containing

polyol. The addition of the nitrogen-containing polyol further suppresses the color change with heat at the curling process.

[0028] Preferably, the nitrogen-containing polyol is tris (2-hydroxyethyl) isocyanurate, tris (3-hydroxypropyl) isocyanurate, or tris (4-hydroxybutyl) isocyanurate. Epoxy compounds other than the nitrogen-containing polyol can be utilized as far as they are acceptable.

[0029] In the present invention, when the amount of the nitrogen-containing polyol is less than 0.01 part by mass, the effect to prevent the color change with heat at the curling process is reduced. On the contrary to this, when the amount thereof is more than 2.0 parts by mass, the thread breakage of the fiber frequently occurs. Accordingly, the amount of the nitrogen-containing polyol is 0.01 to 2.0 parts by mass, preferably 0.02 to 1.0 parts by mass.

[0030] The vinyl chloride fiber of the present invention is formed with melt spinning of the vinyl chloride resin composition containing (a) 100 parts by mass of the vinyl chloride resin, (b) 0.2-5.0 parts by mass of the hydrotalcite thermal stabilizer, (c) 0.2-10.0 parts by mass of the epoxy compound, at a temperature of 170-190°C. The condition of the melt spinning of the present invention provides the long-run melt spinning and stable productivity of the fiber without the color change with heat at the curling process.

[0031] The vinyl chloride fiber of the present invention is manufactured by melt spinning a powder compound or a pellet compound of the vinyl chloride resin composition. The powder compound is prepared by mixing the vinyl chloride resin composition with Henschel mixer or ribbon blender. The pellet compound is prepared by melting the vinyl chloride resin composition. A single extruder, two-color extruder or conical two-color extruder is utilized for manufacturing the vinyl chloride fiber at a temperature of 170-190°C.

[0032] The melt spun vinyl chloride fiber is stretched to 2-4 times at a temperature of 90-120°C in air. The stretched fiber is relaxed under an environment with a temperature of 110-140°C until the length becomes 60-100% of the length prior to the treatment.

[0033] Preferably, the vinyl chloride resin composition contains 0.01-2.0 parts by mass of a nitrogen-containing polyol for the manufacturing of the vinyl chloride fiber. The addition of the nitrogen-containing polyol further suppresses the color change with heat at the curling process in company with the epoxy compound.

## EXAMPLE

### Example 1

[0034] A vinyl chloride resin composition containing: (a) 100 parts by mass of a vinyl chloride resin, which is a blend of 80 parts by mass of a vinyl chloride resin (TAIYO-ENBI, TH-1000), 10 parts by mass of a chlorinated vinyl chloride resin (SEKISUI-KAGAKU, HA-24K), and 10 parts by mass of an ethylene vinyl acetate/vinyl chloride graft copolymer resin (SEKISUI-KAGAKU, TGH-1100), (b) 2 parts by mass of a hydrotalcite thermal stabilizer (KYOWA -KAGAKU, ALCAMIZER-1), (c) 0.8 parts by mass of an epoxy compound (NIHON-USHI, FALPAQ 75ASV), (d) 0.5 parts by mass of a nitrogen-containing polyol (NISSAN-KAGAKU, NF-SE), (e) 0.5 parts by mass of a phosphite compound (ASAHI-DENKA, PEP-8), (f) 0.8 parts by mass of a zinc soap (NISSAN-KAGAKU, NF-12Zn), (g) 1.0 part by mass of a calcium soap (NISSAN-KAGAKU, NF-12Ca), and (h) 0.7 parts by mass of a esters lubricant (RIKEN-BITAMIN, EW-100), is melt spun with a spinning die having a section area of  $0.06\text{mm}^2$ , holes of 120 and die temperature of  $175^\circ\text{C}$  under a throughput rate of 10Kg/hour to manufacture the vinyl chloride fiber having a mean fineness of 135 denier. The vinyl chloride fiber is stretched to 300% in air of temperature  $105^\circ\text{C}$ , and is thermally relaxed at a temperature of  $110^\circ\text{C}$  in air until the length thereof contracts to 75% of the stretched fiber to manufacture the fiber having a mean fineness of 60 denier.

### EXAMPLE 2

[0035] A vinyl chloride fiber is manufactured from a vinyl chloride resin composition without (d) 0.5 parts by mass of a nitrogen-containing polyol (NISSAN-KAGAKU, NF-SE).

### EXAMPLE 3

[0036] A vinyl chloride fibers is manufactured from a vinyl chloride resin composition with an addition of (d) 5 parts by mass of a nitrogen-containing polyol (NISSAN-KAGAKU, NF-SE).

### Comparative Example 1

[0037] The vinyl chloride resin composition containing: (a) 100 parts by mass of the vinyl chloride resin, which is the blend of 80 parts by mass of the vinyl chloride resin (TAIYO-ENBI, TH-1000), 10 parts by mass of the chlorinated vinyl chloride resin (SEKISUI-KAGAKU, HA-24K), and 10 parts by mass of the ethylene vinyl acetate/vinyl chloride graft copolymer resin (SEKISUI-KAGAKU, TGH-1100), (b)

0.1 parts by mass of the hydrotalcite thermal stabilizer (KYOWA -KAGAKU, ALCAMIZER-1), (c) 0.8 parts by mass of the epoxy compound (NIHON-USHI, FALPAQ 75ASV), (e) 0.5 parts by mass of the phosphite compound (ASAHI-DENKA, PEP-8), (f) 0.8 parts by mass of the zinc soap (NISSAN-KAGAKU, NF-12Zn), (g) 1.0 part by mass of the calcium soap (NISSAN-KAGAKU, NF-12Ca), and (h) 0.7 parts by mass of the esters lubricant (RIKEN-BITAMIN, EW-100), is melt spun with the spinning die having the section area of  $0.06\text{mm}^2$ , holes of 120 and die temperature of  $175^\circ\text{C}$  under the throughput rate of 10Kg/hour to manufacture the vinyl chloride fiber having the mean fineness of 135 denier. The vinyl chloride fiber is stretched to 300% in air of temperature  $105^\circ\text{C}$ , and is thermally relaxed at the temperature of  $110^\circ\text{C}$  in air until the length thereof contracts to 75% of the stretched fiber to manufacture the fiber having the mean fineness of 60 denier.

#### Comparative Example 2

[0038] A vinyl chloride fiber is formed similarly to Comparative Example 1 by adding 10 parts by mass of the hydrotalcite thermal stabilizer (KYOWA-KAGAKU, ALCAMIZER), instead of 0.1 parts.

#### Comparative Example 3

[0039] A vinyl chloride fiber is formed similarly to Comparative Example 1 by adding (b) 2 parts by mass of the hydrotalcite thermal stabilizer (KYOWA-KAGAKU, ALCAMIZER-1) and (c) 0.1 parts by mass of the epoxy compound (NIHON-USHI, FALPAQ 75ASV), instead of 0.1 parts and 0.8 parts, respectively.

#### Comparative Example 4

[0040] A vinyl chloride fiber is formed similarly to Comparative Example 1 by adding (b) 2 parts by mass of the hydrotalcite thermal stabilizer (KYOWA-KAGAKU, ALCAMIZER-1) and (c) 20 parts by mass of the epoxy compound (NIHON-USHI, FALPAQ 75ASV), instead of 0.1 parts and 0.8 parts, respectively.

[0041] The vinyl chloride fibers of Examples 1-3 and Comparative Examples 1-4 are evaluated for long-run, color change, frequency of thread breakage, and initial coloring. The result for each Example is given in TABLE 1.



TABLE 1

[0042]	[0043] Example			[0044] Comparative Example			
	1	2	3	1	2	3	4
long-run	◎	◎	◎	×	◎	○	×
color change	◎	○	◎	○	○	×	○
thread breakage	◎	◎	○	×	◎	◎	×
initial coloring	○	○	○	○	×	○	○

[0045] The long-run defines a period of time to change a clogged wire mesh to continue the manufacturing of the fiber. A symbol ◎ means that the thread breakage does not appear over 96 hours continuous melt spinning and the workability and productivity increase, a symbol ○ means that the thread breakage appears little between 48-96 hours but the melt spinning is still possible, and a symbol × means that the thread breakage appears frequently at less than 48 hours and the melt spinning is not possible.

[0046] The color change defines a degree of the change of the color at the curling process. The change of the color is determined by measuring the change of the color of the vinyl chloride fiber before and after a heat treatment with colorimeter (KURASHIKI-BOUSEKI, Colorimeter COLOR-7X). The heat treatment is that the vinyl chloride fiber is stretched and heated in a gear oven at a temperature of 105°C. A b value prior to the heat treatment is a reference value measured under an illuminating and light receiving conditions specified by JIS Z 8722. The reference value b is assigned to b1 and the value after the heat treatment is denoted as b2. When the color change is evaluated by a difference of  $\Delta b = b1 - b2$ , the symbol ◎ means that  $\Delta b < 0.5$  and a visual observation can not detect the color change, the symbol ○ means that  $0.5 \leq \Delta b < 1.0$  and the color change appears a little and the fiber is still utilized for a product, and the symbol × means that  $1.0 \leq \Delta b$  and the visual observation can detect the color change and the fiber is not utilized for the product.

[0047] The thread breakage is a number of the breakage of a single fiber during melt spinning and is converted into a frequency per hour. In the thread breakage frequency (number/hour), the symbol ◎, ○, × means 0, 1-2,  $\geq 3$ ,

respectively. The fibers of the symbols ⊙, ○ are utilized for the product. The fiber of the symbol × is not suitable for the product.

[0048] The initial coloring defines the color of the fiber evaluated with eyes right after the melt spinning. The symbols ○, × stand for that the fibers have no yellow color and yellow color, respectively.

[0049] As seen from TABLE 1, the vinyl chloride fiber of Example 1 shows a distinct result and satisfies all properties requested.

[0050] Example 2 is formed without the polyol of Example 1. Although Example 2 has the color change, it satisfies all properties and capable for the product.

[0051] Example 3 shows the thread breakage more than Example 1 but are adapted to the product.

[0052] Comparative Example 1, which contains less the hydrotalcite thermal stabilizer, shows the frequent thread breakage resulting to a poor long-run.

[0053] Comparative Example 2 shows a poor initial coloring due to the large content of the hydrotalcite thermal stabilizer.

[0054] Comparative Example 3, which contains less the epoxy compound, shows a poor long-run and color change.

[0055] Comparative Example 4, which contains much the epoxy compound, shows the poor thread breakage and long-run.

## INDUSTRIAL APPLICABILITY

A vinyl chloride fiber consists of a vinyl chloride resin composition including (a) 100 parts by mass of a vinyl chloride resin, (b) 0.2-5.0 parts by mass of a hydrotalcite thermal stabilizer and (c) 0.2-10.0 parts by mass of an epoxy compound. An addition of the hydrotalcite thermal stabilizer keeps a long-run and stable melt spinning of the vinyl chloride resin composition and provides less color change to the vinyl chloride fiber with heat at a curling process.

An addition of (d) 0.01-2.0 parts by mass of a nitrogen-containing polyol suppresses further the color change with heat at the curling process in company with the epoxy compound.

A method of manufacturing a vinyl chloride fiber includes the steps of: forming a vinyl chloride resin composition with (a) 100 parts by mass of a vinyl chloride resin, (b) 0.2-5.0 parts by mass of a hydrotalcite thermal stabilizer, and (c)

0.2-10.0 parts by mass of an epoxy compound; and melt spinning said vinyl chloride resin composition at a temperature of 170-190°C. An addition of the hydrotalcite thermal stabilizer keeps a long-run and stable melt spinning of the vinyl chloride resin composition and provides less color change to the vinyl chloride fiber with heat at a curling process.

An addition of (d) 0.01-2.0 parts by mass of a nitrogen-containing polyol to the vinyl chloride resin composition further suppresses the color change of the vinyl chloride fiber with heat at the curling process in company with the epoxy compound.

The vinyl chloride fiber of the present invention provides an artificial hair having a gloss, hue and appearance of human hair utilized for hair ornament products, such as wig, hairpiece, braid, and extension hair.